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SPECIFICATION

1. Title of the Invention: ELECTROLESS PLATED POWDER,
CONDUCTIVE FILLER, AND PRODUCTION PROCESS THEREFOR

3. Detailed Description of the Invention

[Technical Field of the Invention]

The present invention relates to an electroless plated powder and a production process therefor. More particularly, the invention relates to an electroless plated powder including an organic or inorganic core powder and a dense and substantially continuous film formed by electroless plating on the core powder, and a production process therefor. The invention further provides the electroless plated powder as a conductive filler capable of imparting conductivity to synthetic resins or inorganic materials.

[Description of the Related Art]

In general, because of the advancement of technology and development of new applications, electroless plating is widely used today for various substrates, regardless of organic or inorganic materials, and irrespective of the shape and size thereof. In many cases, plates or molded objects are used as a substrate. Since application to powdery or granular core materials is newly developed only recently, there is no established production process therefor, and treatment is only carried out according to the conventionally known methods.

That is, when electroless plating is performed, usually, a method is employed in which a substrate to be plated is immersed in a plating solution prepared in advance and allowed to react for a period of time predetermined by calculation, and then the reaction is terminated.

Even if the substrate to be plated is a powder or powdery object, the same method as that described above is employed. In such a case, the substrate must be rapidly added to a plating solution to perform plating, and after the reaction, termination by filtration, rapid cooling, dilution, or the like of the plating solution must be performed.

When the substrate is a particulate material (powder or powdery material), since the specific surface area is large

compared with the other substrates, the plating reaction rate is exceptionally high.

Consequently, the pH of the plating solution and the individual components vary greatly. Thus, it is extremely difficult to maintain the plating solution stably by adjustment of the pH and resupply of the individual components, which also results in inconstant plating rates.

On the other hand, if the particulate material can be added to the plating solution at once satisfactorily, no problems arise. However, when the particulate material is added slowly to the plating solution, the thickness of the plating film differs between the beginning and the end, resulting in nonuniform thickness.

In particular, in the case of plating of a particulate material, a problem arises in which, if aggregated secondary particles are coated with plating films, during use, the secondary particles are broken to expose uncoated surfaces, and thus coating defects occur.

Consequently, when a particulate material is subjected to plating, it is important to disperse the particulate material as thoroughly as possible so that secondary particles are decreased before applying plating films. However, this cannot be expected in any of conventional methods.

In view of the fact described above associated with

plating of fine particles of such a particulate material, as the method of subjecting a particulate core material to electroless plating, the present inventors have developed a method in which an aqueous suspension of the core material is prepared, and an electroless plating solution is added thereto to apply plating films, and have filed applications for patent (Japanese Unexamined Patent Application Publication Nos. 60-59070, 60-16779, 60-177182, and 60-177183).

In addition, in a method for electroless plating of an organic core material, a technique has also been developed in which, as preliminary treatment, the organic core material is allowed to carry noble metal ions using a noble metal-capturing ability-imparting surface treatment agent, and then subjected to electroless plating to form a metal film having excellent friction resistance (Japanese Unexamined Patent Application Publication No. 61-64882).

[Problems to be Solved by the Invention]

The developed technique described above is significantly improved compared with the conventional electroless plating method in which a powder which is a material to be plated is added to a plating bath prepared in advance, and improvement in quality is recognized. However, there is a room for improvement, and it is still not possible to obtain a metal film that sufficiently satisfies

required performance.

That is, as is well known, in order to perform electroless plating, as preliminary treatment, it is necessary to treat the surface of a material to be plated using palladium chloride so that palladium metal is carried on the surface as catalytic nuclei. In usual cases, a method is employed in which treatment is carried out sequentially or simultaneously with solutions of stannous chloride and palladium chloride, and then plating treatment is carried out. However, it has been experimentally confirmed that the film of the plating metal powder according to this method is extremely nonuniform, a continuous film is not formed, and in order to form such a film, a considerable thickness is required. Moreover, the film has low friction resistance, and plating metal particles are coarse and often have nodular surfaces.

The reason for this is that the palladium catalytic nuclei that control the rate of plating reaction are formed nonuniformly on the surface of the particulate material, and plating metal is deposited on the basis of the nuclei and grown like an island.

Although such a coating state is considerably improved by the method according to the above-described Japanese Unexamined Patent Application Publication No. 61-64882, fundamentally, the similar tendency is present.

Next, when a metal-coated powder is used as a conductive filler, the first advantage is that the specific gravity is low. However, assuming that the metal thickness must be 1,000 Å or more, the particle size of the practicable powder is 1 μm or more. To facilitate the understanding, Table 1 shows the relationship between the metallization ratio (metal/product ratio by weight) and the specific gravity when powders having a specific gravity of 12, each having different particle sizes, are coated with a metal having a specific gravity of 9.0 at a thickness of 1,000 Å.

TABLE 1

| Particle size (μm) | Metallization ratio (%) | Metal/substrate (weight ratio) | Specific gravity |
|------------------------------------|-------------------------------|-----------------------------------|---------------------|
| 50 | 8 | 0.08 | 1.29 |
| 10 | 31 | 0.45 | 1.64 |
| 5 | 48.3 | 0.93 | 2.06 |
| 1 | 84.5 | 5.45 | 4.48 |
| 0.5 | 92.9 | 13.1 | 8.16 |

As is evident from Table 1, although the thickness of the plating metal film is required to be as small as possible from the practical and economical point of view, for that purpose, a uniform and strong film must be formed.

In the present invention, in order to improve the

nonuniform plating film, which is the disadvantage of the conventional technique, and to produce a metal plating powder which is uniform and which has strong covering power, as a result of intensive research effort, development has been successfully made.

[Means for Solving the Problems]

That is, an electroless plated powder provided by the present invention is characterized in that fine metal particles are deposited as a dense and substantially continuous film by an electroless plating method on the surface of an organic or inorganic core material.

Furthermore, a conductive filler of the present invention is composed of the electroless plated powder and is suitable for use in imparting conductivity to substrates, such as synthetic resins.

Furthermore, a process for producing the electroless plated powder and the conductive filler according to the present invention includes a first step (catalyzing treatment) of allowing an organic or inorganic core powder to capture noble metal ions, and reducing the noble metal ions so that the metal is carried on the surface of the core powder, and a second step (electroless plating treatment) of preparing an aqueous suspension by dispersing the core powder which has been treated in the previous step, and adding at least two solutions constituting an electroless

plating solution individually and simultaneously thereto to allow electroless plating reaction to take place.

The present invention will be described in detail below.

First, in the electroless plated powder according to the present invention, as described above, fine metal particles are deposited as a dense and substantially continuous film by an electroless plating method on the surface of a core powder.

Herein, the expression "being dense" means that uniform fine metal particles are in a dense state, in which free metal particles that do not contribute to the formation of the film and nodular deposits of metal particles are hardly present.

Furthermore, the expression "substantially continuous film" means that the surface of the core material is covered by the fine metal particles uniformly in a dense state and the surface of the core material is hardly exposed.

Whether or not such a deposited film is present can be visually recognized by observation with an ordinary microscope or an electron microscope. For example, the photographs in the drawings are each an electron micrograph showing a surface particle structure of a nickel-plated powder having mica as a core material. Figs. 1-a and 1-b relate to the present invention, and Figs. 2 to 5 each relate to plated mica by a conventional plating method.

In the plated mica according to the present invention, metal particles are deposited as a dense and substantially continuous film. In contrast, in the plated mica by the conventional method, the metal particles are coarse and nonuniform, nodular particles are present, and exposure of the surface of the core material is recognized, indicating that a dense and substantially continuous film is not formed.

As described above, since the electroless plated powder of the present invention has strong covering power, friction resistance during use is significantly high compared with a conventional plated powder product. This means that, although depending on the kinds of the core material and the metal or the intended use, the plating film can be as thin as possible. In many cases, advantageously, the thickness is at least 50 Å.

The electroless plated powder according to the present invention is usually a single-layer plated product. As desired, the electroless plated powder may be a multilayer product composed of two or more different kinds of metals. Furthermore, the plating fine metal particles may be crystalline or amorphous depending on the kind thereof or the plating method. Furthermore, for the same reason, the plating metal particles can be magnetic or nonmagnetic.

Examples of the plating metal that can be used include Fe, Cu, Co, Ag, and Au. From the economical point of view,

Ni is the most typical substance. Although Zn and Mn cannot be used alone, they can be used as an alloy.

The core material, which is a material to be plated, is not particularly limited. An organic or inorganic powder dispersible in water, which will be described below, can be used.

The electroless plated powder of the present invention is particularly useful as a conductive filler for synthetic resins, etc. The electroless plated powder can also be used as a catalyst, a pigment, an ornament or the like. In the case of use as a pigment or an ornament, by subjecting the electroless plated powder according to the present invention to heat treatment at a desired temperature, it is possible to obtain a powder assuming beautiful metallic luster with color, such as green, blue, dark blue, or purple. Thus, the applicability thereof can be further expanded.

A process for producing an electroless plated powder according to the present invention will now be described below.

First, a substrate for nickel plating (hereinafter, simply referred to as the "core material") will be described. The first characteristic is that the core material is dispersible in water.

The core material dispersible in water means a core material that can form a suspension in which the core

material is substantially dispersed in water to such a degree that a plating film can be formed on the core material by a usual dispersion means, such as stirring.

Since the core material is dispersible in water, the core material is substantially insoluble in water, and preferably, does not dissolve in or is not modified by an acid or alkali.

Therefore, as long as the core material is substantially insoluble and dispersible in water, the shape and the size thereof are not basically limited. In many cases, the core material is intended as a powdery or granular material. However, the core material may have a specific shape, such as spherical, fibrous, hollow, plate-like, or acicular or an unspecific particle shape attributable to the physical property of the core material.

Consequently, the expression "the core material being a powder" does not have a strict meaning. For example, a plate-like, acicular, or fibrous core material having a high aspect ratio, even with a size of several centimeters, is dispersible, and thus can be used as the core material.

The core material includes any material that can be subjected to electroless plating, regardless of organic or inorganic materials. The material may be any of natural materials and synthetic materials. Of course, the core material is not required to have a chemically homogeneous

structure, and the core material may be crystalline or amorphous.

Examples of such a core material include inorganic core materials, such as metals (including alloys), glass, ceramics, oxides of metals or nonmetals (including hydrates), metal silicates including aluminosilicate, metal carbides, metal nitrides, metal carbonates, metal sulfates, metal phosphates, metal sulfides, metal salts of acids, metal halides, and carbon; organic core materials, such as natural fibers, natural resins, thermoplastic resins, e.g., polyethylene, polypropylene, polyvinyl chloride, polystyrene, polybutene, polyamides, polyacrylates, polyacrylonitrile, polyacetal, ionomers, and polyesters, and thermosetting resins, e.g., alkyd resins, phenol resins, urea resins, melamine resins, xylene resins, silicone resins, epoxy resins, and diallyl phthalate resins. These may be used alone or in combination of two or more.

The second characteristic of the core material is that the core material has noble metal ion-capturing ability or the core material is modified by surface treatment so that at least the surface thereof has the metal ion-capturing ability.

The expression "having noble metal ion-capturing ability" means that noble metal ions can be captured as a chelate or a salt, and one or two or more groups selected

from an amino group, an imino group, an amido group, an imido group, a cyano group, a hydroxyl group, a nitrile group, and a carboxyl group are present on the surface of the core material. Examples of the substance that imparts such capturing ability to the core material itself include organic substances, such as amino resins, nitrile resins, and epoxy resins cured by an amino curing agent, which are suitably used. Examples of amino resins include resins obtained by condensation reaction between an amino compound, such as urea, thiourea, melamine, benzoguanamine, acetoguanamine, dicyandiamide, or aniline, and an aldehyde, such as formaldehyde, paraformaldehyde, acetaldehyde, or glyoxal.

Consequently, in the present invention, when core materials themselves do not have noble metal ion-capturing ability, each core material must be modified by surface treatment so as to have the capturing ability. The modification can be performed according to the method described in Japanese Unexamined Patent Application Publication No. 61-64882. In particular, in the present invention, use of a core material which has been surface-treated with an amino-substituted organosilane coupling agent or an epoxy resin which cures by the action of an amine curing agent is preferred.

Furthermore, as the noble metal ions, palladium ions or

silver ions are particularly preferable.

First step (catalyzing treatment)

When a core material itself has the functional group, catalyzing treatment can be directly performed. When a core material does not have the functional group, surface modification treatment is essential. That is, the core material is dispersed by thorough stirring in water or an organic solvent in which a surface treatment agent is dissolved, and then the core material is isolated and dried. Although the surface treatment agent used varies depending on the physical properties and kinds of the core material, in many cases, the appropriate amount is 0.3 to 100 mg per specific surface area $1 \text{ m}^2/\text{g}$ of the core material. The reason for this is that at about 0.3 mg or less, the amount is insufficient for imparting a modification effect uniformly to the surface. On the other hand, at about 100 mg or more, although a modification effect is obtained, such amount is not economical.

Subsequently, the core material having noble metal ion-capturing ability is dispersed in a dilute acid aqueous solution of a noble metal salt, such as palladium chloride or silver nitrate to allow the core material to capture noble metal ions. In such a case, a concentration of the solution in the range of 0.05 g/l to 1 g/l is sufficient.

Such preliminary treatment is known with respect to

palladium salts. Usually, subsequently, electroless plating treatment is carried out. However, in the present invention, it is important to reduce the noble metal captured on the surface of the core material by a reducing agent used in the electroless plating solution. In the reduction treatment, the reducing agent may be added after the noble metal ion-capturing treatment. Preferably, isolation and water washing are performed after the noble metal ion-capturing treatment, and then the reducing agent as a solution or by itself is added to an aqueous suspension prepared for transfer to the subsequent plating step to complete the catalyzing treatment. Although the amount of the reducing agent added varies depending on the specific surface area of the core material, the appropriate amount is 0.01 to 10 g/l relative to the suspension. In such a case, a complexing agent is preferably present, but is not always essential. The temperature may be normal temperature or elevated temperature and is not particularly limited.

As described above, in the present invention, unlike the conventional technique in which catalytic nuclei is formed by stannous chloride/palladium chloride treatment or chelate treatment simply with palladium chloride, uniform complete catalytic nuclei are formed. Thus, coupled with the action of the subsequent electroless plating step, it is possible to form a strong continuous plating metal film.

Second step (electroless plating treatment)

In this step, it is important to prepare an aqueous suspension in which the core material is dispersed as thoroughly as possible for electroless plating. In a plating film formed on an aggregated core material, untreated surfaces are often exposed during use under friction. In order to avoid this, desirably, the core material is dispersed thoroughly. For the same reason, in the previous step, it is preferable to carry out thorough dispersion treatment.

The dispersibility of the aqueous suspension differs depending on the physical properties of the core material. Desirably, dispersion is performed by a desired means, such as by ordinary stirring or high-speed stirring, or using a shear dispersing device, such as a colloid mill or homogenizer, so as to prepare a suspension in a dispersion state in which agglomerates of the core material are removed as much as possible to allow primary particles to be present predominantly. When the core material is dispersed, for example, a dispersing agent, such as a surfactant, may be used as necessary, as described above. The concentration of the suspension is not particularly limited. If the slurry concentration is low, the plating concentration decreases, and thus the treatment volume increases, which is not economical. On the other hand, if the concentration

increases, the dispersibility of the core material decreases. Thus, a desired slurry concentration is appropriately set depending on the physical properties of the core material. In many cases, the slurry concentration is 10 g/l to 500 g/l, and preferably 20 g/l to 300 g/l. Furthermore, when the core material in the suspension is plated, preferably, the temperature of the suspension is adjusted to the temperature at which plating can be performed, in many cases, at 80°C or higher, in advance so that plating can be performed effectively.

The aqueous suspension of the core material may be prepared using a dispersion medium composed of water alone. In general, the aqueous suspension is preferably prepared using an aqueous solution containing at least one component constituting an electroless plating solution, in particular, using an aqueous solution of a complexing agent. Consequently, since a separation operation is not particularly required after the reduction treatment in the first step, after generation of hydrogen gas is completed, the transfer to the second step can be made continuously.

The above-described at least one component constituting an electroless plating solution refers mainly to a complexing agent, an acid or alkaline agent, and a surfactant. According to need, wastewater of plating can be used.

Furthermore, the complexing agent is a compound having a complexing action on plating metal ions. Examples thereof include carboxylic acids (salts), such as citric acid, hydroxy acetic acid, tartaric acid, malic acid, lactic acid, and gluconic acid or alkali metal salts and ammonium salts thereof, amino acids, such as glycine, amines, such as ethylenediamine and alkylamines; and others, such as ammonium, EDTA, and pyrophosphoric acid (salts). These may be used alone or in combination to two or more. The content of the complexing agent in the suspension is in the range of 1 to 100 g/l, and preferably 5 to 50 g/l.

The pH of the suspension is in the range of 4 to 14. The range varies depending on the plating metal and kinds of the reducing agent used. Examples are shown in Table 2

TABLE 2

| Plating metal | Reducing agent | Proper range (pH) |
|---------------|----------------------|-------------------|
| Nickel | Sodium hypophosphite | 4 to 10 |
| Nickel | Hydrazine | 9 to 13 |
| Nickel | Borohydride compound | 7 to 14 |
| Copper | Formalin | 8 to 12 |
| Gold | Borohydride compound | 8 to 14 |
| Silver | Borohydride compound | 8 to 14 |

A plating solution which is prepared in advance for

electroless plating reaction is gradually added to the aqueous suspension of the core material thus prepared. In such a case, it is necessary to add at least two solutions constituting the electroless plating solution individually and simultaneously to the aqueous suspension to allow plating reaction to take place.

Examples of the metal salt that can be used include nickel salts, such as nickel sulfate and nickel chloride; copper salts, such as copper sulfate and copper nitrate; cobalt sulfate; iron salts, such as iron chloride and iron sulfate; silver salts, such as silver nitrate and silver cyanide; and gold salts, such as gold cyanide and chlorauric acid. As necessary, soluble salts, such as zinc and manganese, can be used as alloy components. These may be used alone or in combination of two or more.

As the reducing agent, for example, sodium hypophosphite, sodium borohydride, potassium borohydride, dimethylamine borane, hydrazine, or formalin is used.

As the other agent, the complexing agent, a pH adjuster, or a brightener, which can be added according to need, is used.

The mixing ratio of the metal salt and the reducing agent varies depending on the combination thereof. In many cases, desirably, the combination and the proper mixing ratio have the relationships shown in Table 3.

TABLE 3

| Metal salt | Reducing agent | Mixing ratio (molar ratio) |
|------------|----------------------|-------------------------------|
| Nickel | Sodium hypophosphite | 1:2 to 3 |
| Nickel | Alkali borohydride | 1:1.5 to 2.5 |
| Nickel | Hydrazine | 1:3 to 5 |
| Copper | Formalin | 1:3 to 5 |
| Gold | Alkali borohydride | 1:1.1 to 1.5 |
| Silver | Alkali borohydride | 1:1.1 to 1.5 |

The concentration of each agent can be set within the saturation concentration and is not particularly limited. However, since low concentration is not economical, the lower limit is naturally limited from the practical point of view. The rate of addition of the agent solution directly affects the plating reaction and is significantly related to the surface area and physical properties of the core material. Thus, in consideration of these, it is necessary to add the agent solution by controlling so that irregularities do not occur in the plating film and a uniform and strong film can be formed. In many cases, it is preferred to add the agent solution gradually at constant rate.

Of course, as necessary, stirring, ultrasonic dispersion treatment, or the like is preferably performed. Furthermore, the temperature is preferably set so as to be

controlled. The electroless plating solution is added to the aqueous suspension and is diluted depending on the size of the volume thereof. Thus, unlike the case in which a substrate to be plated is immersed in a plating bath with an ordinary concentration, it is possible to use at a higher concentration than that of the ordinary plating solution.

By adding the plating solution, plating reaction starts promptly. If the individual agents are added at the proper ratio, all of the metal salt added is reduced and deposited on the surface of the core material. Consequently, the thickness of the plating film can be controlled arbitrarily depending on the amount of addition.

Furthermore, different kinds of metals may be deposited in several layers on the metal-coated powder thus obtained.

In such a case, after the plating reaction is completed, a different metal plating solution is added in the same manner. Alternatively, the reaction mixture is separated by filtration, a new suspension is prepared, and a different metal plating solution is added thereto.

After the addition of the plating solution is completed and no generation of hydrogen gas is confirmed, stirring is continued for a brief period of time to perform aging, and then the plating reaction operation is ended. Subsequently, separation, washing, and drying are performed by known methods, as necessary, followed by pulverization, to give a

product.

[Operation]

In the electroless plated powder according to the present invention, fine metal particles are deposited significantly uniformly and strongly as a dense and substantially continuous film. Consequently, even if mixed with a synthetic resin, a synthetic rubber, or the like, separation of the film or other phenomena do not occur, and satisfactory conductivity can be imparted. Thus, the electroless plated powder can be used directly as a conductive filler.

Furthermore, according to the production process of the present invention, a noble metal chelate captured on the surface of the core powder is reduced to form catalytic nuclei, and this coupled with the action of electroless plating reaction, the electroless plated powder having significantly high quality as described above can be produced with high reproducibility.

[Examples]

The present invention will be described on the basis of the examples below.

Examples 1 to 10

A spherical phenol resin powder (manufactured by Kanebo Ltd.; trade name: Bellpearl R-800) with a true specific gravity of 1.26, an average particle size of 20 μm , and a

specific surface area of 0.5 m²/g (100 g) was added to 1 liter of 0.1 g/l aqueous solution of an aminosilane coupling agent (manufactured by Chisso Corporation; trade name: S-330), and dispersed thoroughly by stirring for about 15 minutes, followed by separation by filtration. Subsequently, drying was performed at a temperature of 105°C to obtain a surface-treated phenol resin powder having chelate ability.

Next, the powder was added to 1 liter of an activating solution composed of 0.1 g/l palladium chloride and 0.1 ml/l hydrochloric acid and dispersed in the same manner, and stirring was performed for 5 minutes. Then, palladium ion-capturing treatment was performed by filtration, repulping, and filtration.

Subsequently, the resulting resin powder was added to each of the complexing agent aqueous solutions shown in Table 4, and thorough dispersion treatment was performed to prepare an aqueous suspension maintained at a temperature of 80°C. Then, 2 g of sodium hypophosphite powder was added to each suspension and dissolved by stirring. Immediately after the addition, bubbling occurred due to generation of hydrogen gas. After the bubbling stopped, the catalyzing treatment was completed.

Subsequently, the electroless plating solutions shown in Table 5, i.e., 86 ml each of the solution **a** and the solution **b**, were added simultaneously at an addition rate of

10 ml/min to each suspension.

After the total amounts of the plating solutions were added, stirring was continued for a brief period of time with the temperature being maintained at 80°C until the generation of hydrogen stopped.

Subsequently, filtration, water washing, filtration, and drying were performed to obtain each nickel-plated resin powder. Each of the filtrates after plating reaction was clear and colorless. Thus, it was found that the plating solution supplied was fully consumed for deposition to the surface of the resin by the plating reaction.

The surface of each plated resin powder was observed with an electron microscope. As a result, each had a uniform and smooth surface composed of fine metal particles. Thus, deposition as a dense and substantially continuous film was confirmed.

TABLE 4

| Example | Kind of complexing agent | Concentration (g/l) | pH |
|---------|--------------------------|------------------------|----|
| 1 | Citric acid | 5 | 7 |
| 2 | Tartaric acid | 10 | 7 |
| 3 | Gluconic acid | 10 | 8 |
| 4 | Malic acid | 10 | 6 |
| 5 | Lactic acid | 10 | 5 |
| 6 | Ethylenediamine | 5 | 7 |
| 7 | Ammonium chloride | 10 | 7 |
| 8 | EDTA | 30 | 9 |
| 9 | Sodium pyrophosphate | 50 | 9 |
| 10 | Glycine | 20 | 8 |

TABLE 5

| Name of agent | concentration (g/l) | Molar ratio |
|---------------------------------|------------------------|----------------|
| Solution a Nickel sulfate | 224 | 1 |
| Solution b Sodium hypophosphite | 226 | 2.5 |
| Sodium hydroxide | 119 | 3.5 |

Examples 11 to 20

The core materials shown in Examples 11 to 17 shown in Table 6 (100 g) was each added to a solution prepared by dissolving an epoxy resin (manufactured by Cemedine Co., Ltd.; trade name: Cemedine 1500) and an amino curing agent, each 1 g, in 500 ml of ethanol, and dispersed under stirring

for 30 minutes. Then, filtration was performed and ethanol was vaporized. The temperature was increased to 80°C. Thus, surface treatment was performed in which the surface of each core powder was coated with the epoxy resin.

The core powders subjected to surface modification with the epoxy resin in Examples 11 to 17 and core powders in Examples 18 to 20 (used without surface modification) were each added to 1 liter of 0.1 g/l silver nitrate aqueous solution, and dispersion was performed by stirring for 30 minutes with a mixer to achieve activation. Then, with respect to each core material, silver ion-capturing treatment was performed by filtration, repulping, and filtration.

Subsequently, core powders were each added to 1 liter of 20g/l EDTA·3Na aqueous solution, followed by thorough dispersion. The temperature was increased to 80°C to prepare each aqueous suspension. Then, 0.5 g of sodium borohydride powder was added to each aqueous suspension and dissolved by stirring. Immediately after the addition, bubbling occurred due to generation of hydrogen gas. When the bubbling stopped after a while, the catalyzing treatment was completed.

Subsequently, a 196.5 g/l copper sulfate solution, a 202.5 g/l formalin solution, and a 157.4 g/l sodium hydroxide solution in the amounts shown in Table 6 were

individually added to each suspension at 60°C under stirring at an addition rate of 3 ml/min.

After the total amount of the plating solution was added, stirring was continued with the temperature being maintained at the same temperature for about 15 minutes until the reaction was completed.

Subsequently, using the known method, by way of the same operation as that in the previous examples, a copper plated powder in which a film was formed on the surface of each core material was obtained. Each of the filtrates after plating reaction was clear and colorless. Furthermore, it was confirmed that each plated powder was a plated product in which fine copper metal particles were deposited as a dense and substantially continuous film.

TABLE 6

| Example | Core material | Shape | Average size | Density (g/cm ³) | Amount of plating solution added (ml) |
|---------|------------------------|-----------|-----------------------------------|---------------------------------|---|
| 11 | Hollow glass particles | Spherical | Diameter 75 µm | 0.66 | 43 |
| 12 | Glass short fiber | Fibrous | Length 3 mm Diameter 9 µm | 2.54 | 64 |
| 13 | Mica | Flaky | Diameter 10 µm | 2.85 | 100 |
| 14 | Alumina powder | Irregular | Diameter 25 µm | 3.95 | 23 |
| 15 | Polyester powder | Irregular | Diameter 5 µm | 1.26 | 345 |
| 16 | Nylon fiber | Fibrous | Length 0.3 mm Diameter 13.6 µm | 1.14 | 92 |
| 17 | Styrene resin powder | Spherical | Diameter 5 µm | 1.05 | 415 |
| 18 | Epoxy resin powder | Spherical | Diameter 7 µm | 1.10 | 283 |
| 19 | Tramine resin powder | Spherical | Diameter 3 µm | 1.35 | 538 |
| 20 | Acrylonitrile | Fibrous | Length 0.3 mm Diameter 13.5 µm | 1.16 | 309 |

Examples 21 to 28

A mica powder with a true specific gravity of 2.89, an average particle size of 4.9 µm, and a specific surface area of 7.0 m²/g (30 g) was subjected to catalyzing treatment as in Example 1. Then, the powder was added to 1 liter of 5 g/l sodium tartrate aqueous solution and dispersed, and the temperature was increased to 70°C.

Subsequently, 3 g of sodium hypophosphite powder was added to the resulting mixture and dissolved. After bubbling due to generation of hydrogen gas stopped, the

catalyzing treatment was completed.

Subsequently, each of a 224 g/l nickel sulfate solution (solution **a**) and a mixed solution (solution **b**) of 226 g/l sodium hypophosphite solution and 85 g/l sodium hydroxide solution was added under stirring in the amount shown in Table 7 at an addition rate of 10 ml/min to the suspension which was prepared by thorough dispersion.

After the total amount was added, stirring was continued with the temperature being maintained at 70°C until the generation of hydrogen stopped.

Subsequently, recovery operation was carried out by the known method. Thus, nickel-plated micas, in which different amounts of the plating solution were added, shown in Table 7 were obtained.

Each of the resulting plated micas was a plated product in which fine nickel metal particles were deposited as a dense and substantially continuous film.

The metallization ratio shown in Table 7 is the calculated value obtained from the amount of the plating solution added. Since each of the filtrates after plating reaction was clear and colorless, it was found that the plating reaction was carried out substantially stoichiometrically.

TABLE 7

| Example | Metallization ratio (metal/substrate + metal) wt% | Amount of each plating solution added (ml) |
|---------|---|--|
| 21 | 10 | 66.6 |
| 22 | 20 | 150.0 |
| 23 | 30 | 257.1 |
| 24 | 40 | 400.0 |
| 25 | 50 | 600.0 |
| 26 | 60 | 900.0 |
| 27 | 70 | 1,400.0 |
| 28 | 80 | 2,400.0 |

Example 29

A methyl methacrylate resin powder with an average particle size of 7 μm , a true specific gravity of 1.42, and a specific surface area of 6.03 m^2/g (30 g) was subjected to palladium ion-capturing treatment as in Example 1.

The resulting resin powder was added to 1 liter of 5 g/l sodium tartrate aqueous solution, and thoroughly dispersed with the temperature being maintained at 80°C to prepare an aqueous suspension. Then, 2 g of sodium hypophosphite powder was added and mixed thereto to complete the catalyzing treatment. A 224 g/l nickel sulfate aqueous solution and a mixed solution of 226 g/l sodium hypophosphite aqueous solution and 119 g/l sodium hydroxide

aqueous solution were added, each in an amount of 612 ml, at an addition rate of 20 ml/l to the suspension under stirring. After the total amounts were added, stirring was continued with the temperature being maintained at 80°C until the generation of hydrogen stopped. Thus, primary coating treatment of nickel plating was carried out. Subsequently, filtration, water washing, and filtration were performed. Then, the filter cake was added to a 50 g/l EDTA-4Na aqueous solution and dispersed thoroughly under stirring, and the temperature was increased to 80°C to prepare an aqueous suspension again.

Subsequently, a 14.83 g/l gold potassium cyanide aqueous solution and a mixed solution of 2.30 g/l sodium borohydride aqueous solution and 12.18 g/l sodium hydroxide aqueous solution were added, each in an amount of 804 ml, at an addition rate of 10 ml/l to the suspension under stirring. After the total amounts were added, stirring was continued for 15 minutes with the temperature being maintained at 80°C. Subsequently, filtration, water washing, and filtration were performed by the known method, followed by drying to obtain a plated powder. The resulting plated powder was a two-layer plated resin powder in which nickel and gold were deposited as dense and substantially continuous films.

Comparative Example 1

A mica powder with a true specific gravity of 2.89, an

average particle size of 4.9 μm , and a specific surface area of 7.0 m^2/g (30 g) was added to 2 liters of an aqueous solution composed of 10 g/l stannous chloride and 1 ml/l hydrochloric acid and dispersed thoroughly under stirring to perform sensitization treatment. Subsequently, after water washing, the treated powder was added to 2 liters of a solution composed of 1 g/l palladium chloride and 1 ml/l hydrochloric acid and dispersed thoroughly under stirring to perform activation treatment for 5 minutes. Thus, catalytic nuclei were formed on the surface of the mica powder.

Subsequently, 20 liters of a plating solution composed of 80 g/l nickel sulfate, 25 g/l sodium hypophosphite, 20 g/l sodium citrate, 10 g/l sodium acetate, and 0.001 g/l lead acetate with pH5 was prepared by increasing the temperature to 60°C. The mica powder which had been subjected to the catalyzing treatment was added to the plating bath and dispersion under stirring was performed. During the reaction, the initial pH of the solution was maintained by the addition of a 160 g/l sodium hydroxide aqueous solution using an automatic controlling device. When the reaction stopped, a 200 g/l sodium hypophosphite aqueous solution was added little by little to allow the reaction to continue. When bubbling did not occur even if the sodium hypophosphite aqueous solution was added, all the addition was stopped. Filtration and water washing were

performed, followed by filtration and drying to give a nickel-plated mica powder.

Comparative Example 2

A mica powder with a true specific gravity of 2.89, an average particle size of 4.9 μm , and a specific surface area of 7.0 m^2/g (30 g) was subjected to catalyzing treatment as in Comparative Example 1. Subsequently, the powder was added to 1 liter of 20 g/l sodium tartrate aqueous solution, and dispersed at a temperature of 70°C to prepare an aqueous suspension.

Subsequently, 3 g of sodium hypophosphite powder was added and dissolved under stirring. Soon after the addition, bubbling occurred. After the bubbling stopped in a short time, a 224 g/l nickel sulfate solution (solution **a**) and a mixed solution (solution **b**) of 226 g/l sodium hypophosphite and 119 g/l sodium hydroxide (10.72 liters each) were added individually and simultaneously to the suspension under stirring at an addition rate of 10 ml/min. After the total amounts were added, stirring was continued with the temperature being maintained at 70°C until the generation of hydrogen stopped. Subsequently, filtration and water washing were performed, followed by filtration and drying to give a nickel-plated mica powder.

Comparative Example 3

A mica powder with a true specific gravity of 2.89, an

average particle size of 4.9 μm , and a specific surface area of 7.0 m^2/g (30 g) was subjected to catalyzing treatment as in Example 1. Subsequently, electroless nickel plating was performed using a plating solution prepared under the same conditions as those in Comparative Example 1 to give a nickel-plated mica powder.

Comparative Example 4

A mica powder with a true specific gravity of 2.89, an average particle size of 4.9 μm , and a specific surface area of 7.0 m^2/g (30 g) was subjected to catalyzing treatment by capturing of palladium ions under the same conditions as those in Example 1.

The powder was added to 1 liter of 5 g/l sodium tartrate aqueous solution, and dispersed at a temperature of 70°C to prepare an aqueous suspension. Subsequently, a 224 g/l nickel sulfate solution (solution **a**) and a mixed aqueous solution (solution **b**) of 226 g/l sodium hypophosphite and 119 g/l sodium hydroxide (20 ml each) were added individually and simultaneously to the suspension under stirring to initiate plating reaction. Immediately after this, the solution **a** and the solution **b** (2.4 liters each) were added in the same manner. After the total amounts were added, stirring was continued with the temperature being maintained at 70°C until the generation of hydrogen stopped. Subsequently, filtration, water washing, filtration, and

drying were performed to give a nickel-plated mica powder.

Analysis of Nickel film

Nitric acid was added to each of the nickel-plated powders obtained in the examples and comparative examples to dissolve the film. The resulting solution was analyzed to actually measure nickel and phosphorus in the film. The results are shown in Table 8.

TABLE 8

| | Core material | Ni(Ni/Ni+core material) (wt%) | P(P/Ni+P) (wt%) | Calculated thickness (Å) |
|-----------------------|---------------------|----------------------------------|--------------------|-----------------------------|
| Example 1 | Phenol resin powder | 4.00 | 3.1 | 100 |
| Example 2 | Phenol resin powder | 4.10 | 2.8 | 100 |
| Example 3 | Phenol resin powder | 4.10 | 2.7 | 100 |
| Example 4 | Phenol resin powder | 4.05 | 3.0 | 100 |
| Example 5 | Phenol resin powder | 4.04 | 3.0 | 100 |
| Example 6 | Phenol resin powder | 4.00 | 3.2 | 100 |
| Example 7 | Phenol resin powder | 4.10 | 2.7 | 100 |
| Example 8 | Phenol resin powder | 4.01 | 3.0 | 100 |
| Example 9 | Phenol resin powder | 4.06 | 2.9 | 100 |
| Example 10 | Phenol resin powder | 4.08 | 2.8 | 100 |
| Example 21 | Mica powder | 9.9 | 3.5 | 20 |
| Example 22 | Mica powder | 19.7 | 3.3 | 40 |
| Example 23 | Mica powder | 29.8 | 2.9 | 70 |
| Example 24 | Mica powder | 39.5 | 2.8 | 110 |
| Example 25 | Mica powder | 49.4 | 2.8 | 170 |
| Example 26 | Mica powder | 59.6 | 2.7 | 260 |
| Example 27 | Mica powder | 69.1 | 2.8 | 390 |
| Example 28 | Mica powder | 79.6 | 2.7 | 660 |
| Comparative Example 1 | Mica powder | 73.6 | 9.8 | 800 |
| Comparative Example 2 | Mica powder | 94.0 | 2.7 | 2,600 |
| Comparative Example 3 | Mica powder | 73.8 | 9.5 | 800 |
| Comparative Example 4 | Mica powder | 79.4 | 2.7 | 660 |

Measurement of conductivity

Using BRABENDER PLASTOGRAPH, 35.7 ml (32.13 g) of polypropylene (manufactured by Mitsubishi Yuka Co., Ltd.: MA-4, PP homopolymer) and 6.3 ml of nickel-plated mica test powder were mixed for 5 minutes at 220°C and 30 R.P.M. The resulting mixture was taken out, stretched into a plate with thermal rollers, and further formed into a plate with a thickness of 1 mm by hot pressing. With respect to a test piece obtained by cutting the resulting plate to a size of 30 × 60 mm, electrical resistance was measured to obtain resistivity of each of the products in the examples and comparative examples to evaluate the conductivity. The results thereof are shown in Table 9.

TABLE 9

| | Thickness of Ni plating film (Å) | Resistivity (Ω - cm) |
|-----------------------|-------------------------------------|-------------------------|
| Example 21 | 20 | 2.5×10^4 |
| Example 22 | 40 | 4.8×10 |
| Example 23 | 70 | 2.7 |
| Example 24 | 110 | 1.2×10^{-1} |
| Example 25 | 170 | 4.5×10^{-2} |
| Example 26 | 260 | 2.8×10^{-2} |
| Example 27 | 390 | 2.7×10^{-2} |
| Example 28 | 660 | 2.8×10^{-2} |
| Comparative Example 1 | 800 | ∞ |
| Comparative Example 2 | 2,600 | ∞ |
| Comparative Example 3 | 800 | 3.0×10^{-3} |
| Comparative Example 4 | 660 | 5.2×10^2 |

As is evident from Table 9, in the products in the comparative examples, the amount of nickel plating is significantly large compared with the products in the examples, and in spite of the large thickness, separation of the plating film occurs during mixing with the resin. As a result, the resistivity of the resin increases, and it is not possible to obtain an effective conductive resin. On the other hand, the products in the examples each impart conductivity effectively to the resin.

As a result, it is conformed that in the plating powders according to the present invention, a plating film is strongly formed on the core material, and thus the powders can be used as an excellent conductive filler.

[Advantages]

The plated powder according to the present invention has a significantly uniform and strong plating film compared with the conventional plated powder. That is, the plated powder is an electroless plated powder having high bonding power in which a dense and substantially continuous film composed of fine metal particles is deposited and no nodular particles or plating irregularities are present. The plated powder can be used in various applications, such as for conductive fillers.

Furthermore, in the process according to the present invention, unlike the conventional catalytic nuclei composed of colloidal or simply chelated palladium, catalytic nuclei are formed by reduction of the noble metal chelate captured on the surface of the material to be plated. Therefore, coupled with the plating reaction on the basis of the addition method, the plated powder can be industrially advantageously produced with high reproducibility.

Consequently, according to the present invention, since the metallization ratio can be set as low as possible, i.e., a strong plating film of a submicron order can be imparted,

it is possible to obtain a plated powder with a low specific gravity.

This assures that, coupled with the fact that various core materials can be used, it is possible to provide a uniform conductive material in which separation does not occur when mixed as a conductive filler into a paint, a synthetic resin, a synthetic rubber, or the like.

4. Brief Description of the Drawings

The drawings are each an electron micrograph showing a surface particle structure of a plating film in an electroless nickel-plated mica. Fig. 1-a relates to the example of the present invention ($\times 500$), Fig. 1-b is an enlarged photograph ($\times 5,000$) thereof. Fig. 2 relates to the product obtained in Comparative Example 1 ($\times 10,000$), Fig. 3 relates to Comparative Example 2 ($\times 10,000$), Fig. 4 relates to Comparative Example 3 ($\times 10,000$), and Fig. 5-a ($\times 500$) and Fig. 5-b ($\times 5,000$) relate to Comparative Example 4 which corresponds to Fig. 1-a and Fig. 1-b.

Claims

1. An electroless plated powder comprising an organic or inorganic core powder and fine metal particles deposited as a dense and substantially continuous film on the surface of the core powder by an electroless plating method.

2. The electroless plated powder according to Claim 1, wherein the continuous film is a multilayered film composed of different kinds of metals.
3. The electroless plated powder according to Claim 1, wherein the continuous film has a thickness of at least 50 Å.
4. A conductive filler comprising the electroless plated powder according to Claim 1.
5. A process for producing an electroless plated powder and a conductive filler comprising a first step (catalyzing treatment) of allowing an organic or inorganic core powder to capture noble metal ions, and reducing the noble metal ions so that the metal is carried on the surface of the core powder, and a second step (electroless plating treatment) of preparing an aqueous suspension by dispersing the core powder which has been treated in the previous step, and adding at least two solutions constituting an electroless plating solution individually and simultaneously thereto to allow reaction to take place.
6. The process for producing the electroless plated powder and the conductive filler according to Claim 5, wherein the core powder has a specific shape, such as substantially

spherical, fibrous, hollow, plate-like, or acicular, or an irregular particle shape.

7. The process for producing the electroless plated powder and the conductive filler according to Claim 5, wherein a substance at least a surface of which has metal ion-capturing ability or a substance to which metal ion-capturing ability is imparted by surface treatment is used as the core powder.

8. The process for producing the electroless plated powder and the conductive filler according to Claim 5 or 7, wherein the core powder at least a surface of which has metal ion-capturing ability is a resin powder comprising one or two or more resins selected from epoxy resins, acrylonitrile resins, and amino resins.

9. The process for producing the electroless plated powder and the conductive filler according to Claim 5 or 7, wherein the core powder to which metal ion-capturing ability is imparted by surface treatment is a substance surface-treated with an amino-substituted organosilane coupling agent and/or an epoxy resin which cures by the action of an amine curing agent.

10. The process for producing the electroless plated powder and the conductive filler according to Claim 5, wherein the catalyzing treatment of the first step is carried out employing any reducing agent used in electroless plating reaction.

11. The process for producing the electroless plated powder and the conductive filler according to Claim 5, wherein the aqueous suspension in the second step is prepared using an aqueous solution containing at least one component constituting the electroless plating solution.